

# Distribution of dangling bond pairs on partially hydrogen-terminated Si(100) surface observed by scanning tunneling microscopy

Ru-Ping Chen, Deng-Sung Lin \*

*Institute of Physics, National Chiao-Tung University, 1001 Ta-Hsueh Road, Hsinchu 300, Taiwan*

## Abstract

Hydrogen recombinative desorption from a Si<sub>2</sub>H<sub>2</sub> monohydride dimer on the Si(100) surface regenerates a dangling bond (DB) pair on the dimer. In this paper, we investigated the spatial distribution of the regenerated DB pairs on the Si(100)-2 × 1:H and disilane-passivated Si(100) surface using elevated temperature scanning tunneling microscopy (HT-STM) in the temperature range between 590 and 622 K. Experimental results indicate that the ends of one-dimensional (1D) monohydride dimer islands are preferred sites for DB pairs and a repulsive interaction occurs between two neighboring DB pairs in the same dimer row. © 2000 Elsevier Science B.V. All rights reserved.

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An ideal semiconductor surface unavoidably holds a high density of dangling bonds (DBs), which possess a sizeable amount of excess energy. The total energy lowering by reducing the density of surface DBs plays an essential role in driving the surface reconstruction, step morphology and all surface reactions (for a review see Ref. [1]). Therefore, understanding the nature of DBs and their mutual interaction is essential to the physics and chemistry of semiconductor surfaces. To this end, the Si(100)-2 × 1 surface has been the model system of extensive experimental and theoretical studies [2]. On an unreconstructed Si(100) surface, each surface atom is bonded to two atoms in the second layer and has two DBs. The 2 × 1 recon-

struction reduces the surface energy by forming dimers: alternate rows of surface atoms move towards each other to establish a strong  $\sigma$  bond per dimer, thereby rebonding half of the DBs. Self-consistent calculations indicated that the two remaining DBs in a dimer, referred to herein as the DB pairs, are also rebonded by a weak  $\pi$  interaction [3]. Boland thoroughly elucidated the  $\pi$  interaction between two DBs while examining the adsorption of atomic hydrogen [4]. According to his results, two hydrogen atoms adsorbed on one side of the two dimers tend to pair up due to an attractive interaction between the two unsaturated DBs on the other side of the two dimers.

McEllistrem et al. [5] observed apparent concerted motion of DB pairs, suggesting that an attractive interaction occurs between individual DB pairs. Another scanning tunneling microscopy

\* Corresponding author. Fax: +886-3-572-0728.  
E-mail address: dslin@cc.nctu.edu.tw (D.-S. Lin)

(STM) investigation obtained 60% hydrogen desorption on Si(100)-2×1:H after 5 min of desorption at 710 K [4]. According to their results, delineated DB regions tend to be separated from hydrogenated ones. Assuming that the experimentally observed distribution represents an equilibrium distribution, this suggests an energetic preference for clustering of DB pairs or Si<sub>2</sub>H<sub>2</sub> monohydride dimers. Although incorporating effective nearest-neighbor attractive interactions between Si<sub>2</sub>H<sub>2</sub> monohydride dimers, Monte Carlo simulation [6] failed to reproduce the cluster size distribution observed by STM.

In this study, elevated temperature STM is used to provide a real-space view of the distribution of DB pairs generated by hydrogen thermal desorption from H-terminated Si(100) surfaces in the temperature range 590 to 622 K. Previous investigations [4,7–9] revealed that hydrogen desorbs randomly and recombinatively from the Si<sub>2</sub>H<sub>2</sub> monohydride dimers on the hydrogen-covered Si(100) surfaces. The desorption of a H<sub>2</sub> molecule from a Si<sub>2</sub>H<sub>2</sub> monohydride dimer leaves behind a dimer, which consists of a DB pair. Herein, both atomic hydrogen and disilane (Si<sub>2</sub>H<sub>6</sub>) are used as hydrogen precursors. Annealing the hydrogen- and disilane-saturated Si(100) surfaces at elevated temperatures gradually regenerates DB pairs and ultimately drives them to reach a thermal equilibrium distribution. Disilane deposits both hydrogen and silicon atoms, producing 1D monohydride dimer islands at about 640 K. Compared with a flat surface, the freedom of DB pairs on short 1D dimer islands is substantially reduced; the entropy effect leading to random spatial distribution of DB pairs is thus largely depressed. Contrary to a previous suggestion that a DB pair attracts another, results in this study demonstrate that DB pairs tend to keep a distance from each other, implying that an effectively repulsive interaction occurs between two neighboring DB pairs.

Experiments were performed using commercial elevated temperature STM. The Si(100) samples (B-doped, 10 Ω cm) were outgassed for more than 12 h at 900 K. The clean Si(100)-2×1 surfaces were prepared by direct Joule heating at ~1400 K with subsequent radiation quenching. Infrared

optical pyrometers were used to measure the sample temperature. Atomic hydrogen was produced by backfilling the chamber in the presence of an 1800 K tungsten filament. Typical dosing time to obtain the Si(100)-2×1:H surface is 200 s at a hydrogen pressure of 1×10<sup>-6</sup> Torr. Disilane (ultra-high purity grade) was introduced into the chamber through a precision leak valve. To minimize interactions between the surface and the tip [5], the surface was normally scanned at -1.5 to -2 V sample bias and <0.3 nA tunneling current.

Dosing atomic hydrogen on a clean Si(100)-2×1 surface at 590 K yields a Si(100)-2×1:H surface composed of symmetric monohydride dimer units (Fig. 1a). The π bond in a bare Si dimer is replaced by two strong Si-H σ bonds, while the dimer structure remains intact upon adsorption of hydrogen atoms. Fig. 1b and c, taken at 590 K, displays the Si(100)-2×1:H

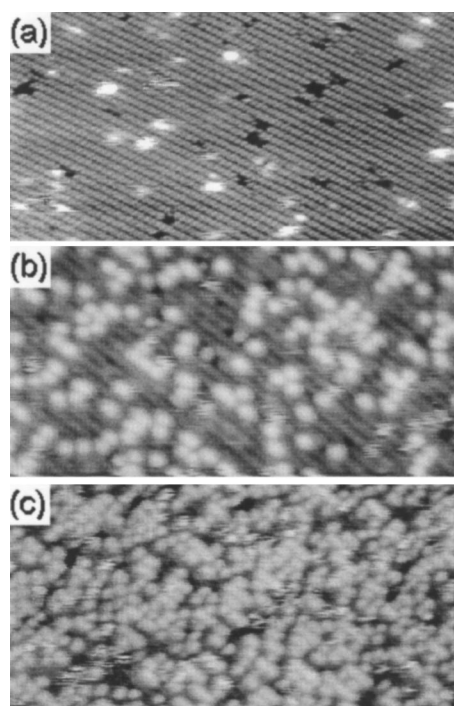


Fig. 1. (a) Filled state STM image of the Si(100)-2×1:H and the same surface after (b) 210 s of H<sub>2</sub> desorption at 668 K and (c) 10 s at 690 K. All images are obtained at 590 K. The bright protrusions centered along the dimer rows are DB pairs.

monohydride surface followed by 210 s annealing at 668 K and 10 s at 690 K, respectively. The bright protrusions appear to be centered along the dimer rows; they are DB pairs where their  $\pi$  bonded states have a high efficiency of electron transfer between the tip and the surface. The coverages of the DBs are 0.12 and 0.35 ML (1 ML =  $6.8 \times 10^{14}$  atoms/cm<sup>2</sup>) for Fig. 1b and c, respectively. As evidenced by the fluxial features of some DB pairs [5,10], the DB pairs are mobile enough to reach equilibrium distributions at 590 K. Most DB pairs in Fig. 1 appear isolated from each other; only some short DB chains can be discerned in Fig. 1c. Large islands of paired DBs were not observed and paired DB sites such as those in Fig. 1 remained randomly distributed throughout several hours of continuous STM observation at 590 K, either on the same areas or different ones. This phenomenon suggests two possibilities: (1) although a small attractive interaction occurs between two individual paired DBs, the configuration entropy of the system causes DB pairs to separate from each other; (2) an effective repulsive interaction occurs between two DB pairs. The second case seems evident since, as the STM observation suggests, DB pairs at low coverages do not form clusters when encountering each other during thermal diffusion. However, the spatial distribution of DB pairs on Si(100)- $2 \times 1$ :H alone does not provide a conclusion about the nature of their mutual interaction, in that they are free to move over the entire surface. Elucidating the nature of the interaction between DB pairs requires minimizing the configuration entropy of the system, i.e. the freedom of DB pairs.

Since the diffusion of DB pairs occurs predominantly along dimer rows [5], the entropy minimization can be accomplished by partially desorbing H<sub>2</sub> from short 1D  $2 \times 1$ :H monohydride dimer trains, as demonstrated in Fig. 2. A previous study [11] revealed that monohydride dimer trains can be obtained on a Si(100) surface by dosing 15 L disilane at 643 K, as shown in Fig. 2a. The surface prepared in this manner is largely H-terminated on both the substrate and the 1D dimer islands running perpendicular to the dimer rows of the substrate. The disilane-saturated surface was main-

tained at 622 K for 77, 132, 263, 416, and 762 min for Fig. 2b–f, respectively. At this temperature, hydrogen slowly desorbs, gradual increasing the population of the paired DB sites (bright, desorption sites) on both the substrate and 1D islands. As evidenced from Fig. 2a–c, regenerated DB pairs on 1D dimer islands occupy initially the ends of 1D dimer islands, suggesting that the ends of 1D dimer islands serve as energetically favored sites for DB pairs. In Fig. 2d, about half or less than half of the hydrogen on most 1D dimer islands and on the substrate dimer rows has desorbed; most DB pairs left behind on 1D dimer islands and on the short substrate dimer strings between 1D dimer islands appear mostly isolated. In particular, the 1D dimer islands indicated by white arrows in Fig. 2d–f exhibit cocoon shapes; the distance between two protrusions (the regenerated DB pairs) is  $2a_0$ . Close inspection of Fig. 2c shows that DB pairs on the dimer islands slightly favor the ends of substrate dimer rows over the end of troughs between substrate dimer rows. However, the difference for the two configurations is not much, suggesting that the strain field due to the substrate does not dominate the spatial distribution of DB pairs on the 1D islands. By assuming that no interaction occurs between the DB pairs, the probability for the distribution of DB pairs, such as that indicated by the arrow in Fig. 2e for a 1D island with seven dimers in length, is less than 1%. However, most of the 1D islands of this kind exhibit the same cocoon-shaped distribution in our STM observation.

The apparent distribution of DB pairs is not due to charge redistribution between DBs [12], since the ordinary dimer islands can be observed in Fig. 2f after more DB pairs are regenerated. The distribution of DB pairs in Fig. 2 strongly suggests that the effective interaction between two DB pairs in the same dimer row is, in fact, repulsive. Two neighboring DB pairs in the same dimer row have fewer strained second-layer atoms than two distant ones. The respective nearest-neighbor interaction due to local strain effects is supposed to be attractive and, therefore, unlikely to drive the neighboring DB pairs in the same dimer row to separate. Notably, the spatial charac-

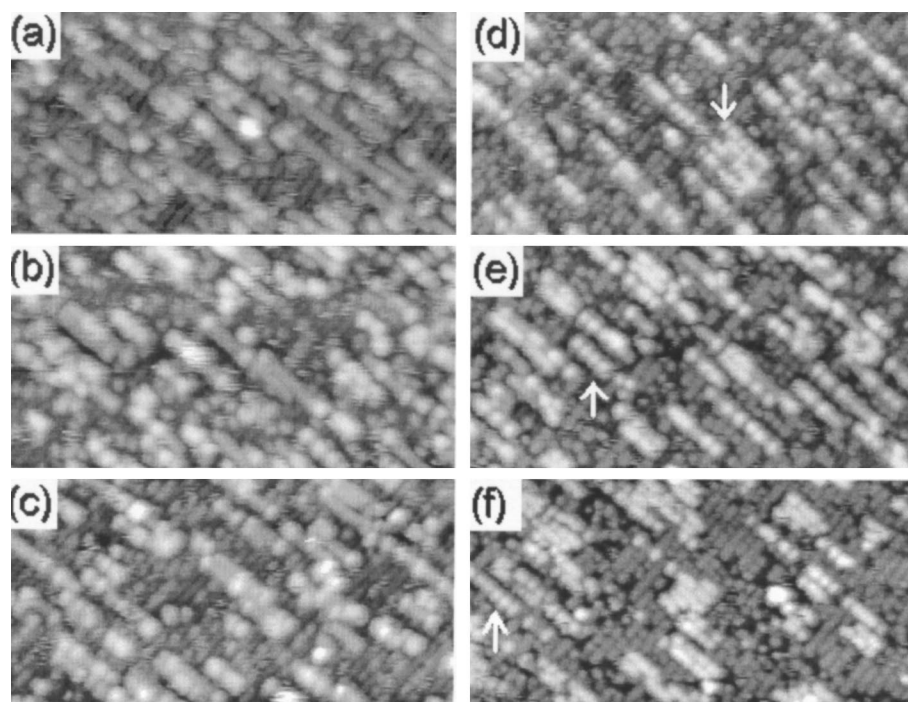


Fig. 2. Real-time STM images obtained at 622 K for (a) the H-terminated surface with 1D monohydride islands prepared by exposing a clean Si(100)- $2 \times 1$  surface to 15 L disilane at 643 K and the same surface after (b) 77, (c) 132, (d) 263, (e) 416 and (f) 762 min of annealing at 622 K. Note that the DB pairs on the 1D islands indicated by arrows are separated by  $2a_0$ .

teristics of the  $\pi$  bond state observed in the STM images on the Si(100)- $2 \times 1$ :H surface after partial hydrogen desorption exhibit a large extent of nearly  $3a_0$ , where  $a_0 = 3.85 \text{ \AA}$  [4]. Also, theoretical [13] and experimental [14] results demonstrated that electronic interdimer interactions are present along the dimer row direction for the clean Si(100)- $2 \times 1$  surface. Thus, one could infer that an electronic interaction occurs between two nearby DB pairs. Each of the two broken bonds on the two surface Si atoms in a dimer is rebonded to form a  $\sigma$  and a  $\pi$  bond. Intuitively, the electrons between two neighboring saturated bonds have steric repulsive Coulomb interaction. Therefore, the repulsive force between two neighboring Si—Si dimers in a row is anticipated. The flat  $2 \times 1$  surface is essentially a large 2D dimer island. The conclusion drawn here for 1D dimer trains should also be applied to the flat surface, since DB interaction on the Si(100) surface involves predominantly the same dimer row. When the desorption of surface

hydrogen exceeds 50% on the Si(100)- $2 \times 1$ :H surface, clusters and/or patches of DB pairs will certainly form for obvious statistical reasons, as confirmed in Ref. [4]. However, the exact thermodynamically favorable spatial distribution of DB pairs at high coverage, complicated by the possible effect of non-local strain fields [4], is unclear.

In summary, we have generated DB pairs by partially desorbing  $\text{H}_2$  molecules from the Si(100)- $2 \times 1$ :H,  $\text{Si}_2\text{H}_6$ -saturated Si(100) surfaces and observed their equilibrium distribution at elevated temperature. Results in this study demonstrate that DB pairs tend to keep a distance from each other and suggest a repulsive interaction between two neighboring DB pairs. The electronic interaction between DB pairs provides further insight into the nature of the clean Si(100)- $2 \times 1$  surface. The repulsive force also implies that the hydrogen desorption barrier on hydrogen-covered Si(100)- $2 \times 1$  at high coverage is slightly lower than that at low coverage.

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